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Physico-mechanical properties of chemically treated polypropylene rice straw bio-composites

M. Bassyouni[1], I. Taha[2], Shereen M.-S. Abdel-hamid[3] and L. Steuernagel[4]

Abstract

Rice straw is causing in many countries severe environmental problems in terms of black clouds caused by the incineration process. Hence, among other reasons, the incorporation of ground rice straw as a filler and reinforcement material for polymers is of advantageous. In this study, Egyptian rice straw was used to reinforce commercial polypropylene and laboratory prepared maleic anhydride-grafted PP with the fill grades between 5 wt% and 30 wt%. Rice straw PP composites show an improved Young's modulus at increased fill grades, against a decrease in tensile strength. The addition of 1% maleic anhydride per 1 g of rice straw as a compatibilizing agent caused further amelioration of the fiber/matrix bonding leading to improved mechanical behavior, which was also assessed using scanning electron microscopy. Additional assessments were made via thermographic analysis and density measurements.

Keyword

biocomposites, maleic anhydride, rice straw, thermal degradation

Introduction

By no doubt, the issue of using natural fibers as reinforcement for polymer composites has been standing in the limelight of research in the past decade.[1] Their power to compete with the widely spread synthetic fibers derive from their specific properties, price, health advantages, sustainability and renewability. The natural origin of the fibers, does however not only contribute to quality improvement of the final product, but also allows for the reduction of hazards during production, which is expressed in terms of lower pollution levels, reduced energy consumption, and neutralizing CO_2 emissions (amount of CO_2 emitted during production does not exceed that neutralized by the plant during growth).[2–5] Moreover, the use of natural fibers in certain countries where it is of common practice to incinerate vegetable waste, the integration of these fibers as fillers, or reinforcement of polymer composites brings along an added value in addition to further environmental salvation. This is a burden that is especially faced with rice straw as a vegetation side product. However, literature does not often cite research on the use of rice straw as a natural reinforcement of polymer composites.[6]

The use of natural fibers, however, involves several obstacles. Generally, lignocellulosic fibers are incompatibles with hydrophobic polymers, due to their inherent hydrophilic nature, developed from the presence of hydroxyl groups ready to form hydrogen bonds with water molecules.[5,7,19] Even if a successive bonding could be achieved, the high water absorption of the cellulose fibers would cause swelling and in turn dimensional instability that would promote poor processability and the development of cracks and herewith poor mechanical properties of the composite. In order to

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overcome these drawbacks, next to the physical (corona, plasma) and chemical treatments (acetylation, isocyanation) of the fiber's surface, grafting, and the addition of compatibilizing agents to the polymer matrix are common techniques.[8,9] A strong adhesion at the interface is herewith warranted, allowing for proper stress transfer and load distribution between the two phases.

Especially, the use of fiber-grafted polymer chains and block copolymers as compatibilizing agents appear to offer the greatest promise, as has been demonstrated with maleic anhydride grafted polypropylene (MAPP). This copolymer is capable of reacting with the hydroxy functionality of the wood surface while, according to Sherif et al.,[1] co-crystallizing with the polypropylene matrix.

Accordingly, the use of MA-grafted PP was used in this study to achieve the desired bonding between reinforcing rice straw fibers and commercial polypropylene.

Experimental work

Material

Rice straw was directly obtained from the fields of El-Sharkeya governorate in Egypt. The fibers where then ground in a ball mill at 250 rpm for 4 h. Homopolymer PP developed for thin wall high speed injection molding is used as the host matrix, and is supplied by DOW GmbH (melt flow rate = 52 at 230°C/2.16 kg and specific density of 0.9). MA (M625 powder) and peroxide 90% 'Luperox 101' are supplied by Sigma–Aldrich. Trimethoxyvinylsilane (molecular wt = 148.23 g/mol) and AA (molecular wt = 72.06 g/mol) are both supplied by Merck Schuchardt.

MAPP was prepared according to George et al.,[8] where the compatibilizer MAPP is prepared by mixing PP with maleic anhydride in a weight ratio of 98:2, and then 1% of the peroxide catalyst is added. The mixture is dry blended and fed through the hopper at 5 kg/h. The mixture is extruded at 180°C and 200 rpm. Effective extruder cylinder length is 40 mm to cylinder diameter 16 mm. The output material is water cooled and pelletized.

Matrix preparation and composite production

The prepared pellets of the prepared MAPP are mechanically mixed in a rotating vessel with PP in 1% (w/w) MAPP for each 10 grams of rice straw. Composites are developed by means of a PolyLab system kneader from Thermo Haake (Rheomix 600P), where the polymer is first melted and homogenized at 50 rpm for 5 min, then further kneaded after the addition of ground rice straw (1.5–2 mm in length) for another 25 min up to constant torque, to ensure homogeneous fiber dispersion in the matrix. The compound is then shredded and injection molded according to the processing parameters given in Table 1 using Allrounder 220C 600-250, Arburg, Lossburg, Germany.

Test methods

Density measurements. The Archimedean principle was applied for determining the specific gravity of ten $20 \times 12\,\mathrm{mm}^2$ injection molded rice straw polypropylene (RPP) and rice straw maleic anhydride-grafted polypropylene (RMAPP) samples. The samples were weighed in air (W(a)) and in degassed distilled water ($W(H_2O)$), and the density (ρ) calculated according to Equation (1), where ρ (H_2O) is the water density:

$$\rho = \frac{W(\mathrm{a}) \cdot \rho(\mathrm{H_2O})}{W(\mathrm{a}) - W(\mathrm{H_2O})} \tag{1}$$

Water absorption. Water absorption tests according to DIN 53495 by immersing five samples in distilled water at 23°C for 24 h, where RPP and RMAPP samples were taken out every 60 min, surface water droplets are removed using a fine tissue, weighed, and returned into the distilled water within 1 min. Weight percent change was then recorded with respect to time.

Thermogravimetric analysis. Thermogravimetric measurements were carried out on RPP and RMAPP injection molded composite samples using a Hi Res TGA 2950 thermodynamic Analyzer from TA Instruments under nitrogen flow. Measurements were performed at a heating rate of 5°C/min from room temperature to 800°C.

Mechanical testing. Matrix and composites are characterized for tensile and impact behavior, applying DIN EN ISO 527–2/5A/2 and EN ISO 179–1, respectively. Tensile tests are conducted on a Zwick Universal Testing Machine at a crosshead speed of 2 mm/min.

Table 1. Main injection parameters (optimum conditions according to own trials)

Injection pressure (bar)	800
Holding pressure (bar)	80% of injection pressure
Mold temperature (°C)	40
Barrel zone temperature (°C)	30–170–175–180–190
Injection speed (ccm/s)	22
Feeding volume (ccm)	3
Cooling time (s)	10

The reaction force and displacement are recorded and the stress, strain, and Young's modulus are determined.

Scanning electron microscopy. Samples were mounted onto holders using double-sided electrically conducting carbon adhesive tabs. The specimens were coated with gold using a Cressington sputter coater at a voltage of 20 mA for 100 s and the samples were observed with a SC44 Camscan scanning electron microscope.

Results and discussion

Density

The density of the RPP composites as a function of fiber content is illustrated in Figure 1. As anticipated by the Rule of Mixtures (ROM), the density linearly increases with increasing fiber content, ranging between 0.9 and 1.01 g/cm^3 for pure PP and 30% filled RPP composite, respectively. The addition of MA as a coupling agent led to increse in the composite density 0.5%. Taking 20% fiber content as an example, 0.975 gcm^3 was measured in case of RPP compared to 0.970 g/cm^3 in case or RMAPP.

Water absorption behavior

Results of water absorption testing for virgin PP and RPP composites are presented in Figure 2. It can be clearly seen that all composites tend to rapidly absorb water during the initial period of being immersed into water, whereas the rate of water absorption decreases with time, until it reaches a saturation limit after approximately 24 h. A further observation is the increase in water absorption rate with increased fiber content. Such observations have also been made by Djidjelli et al.[11] and are related to the water intake of natural fibers through the hollow central (the lumen), which gives access to water penetration by capillary action. This is of course also to be seen in addition to the general water uptake of natural fibers based on their hydrophilic nature.[1,11,12]

The effect of the addition of maleic anhydride on the water absorption behavior can be observed in Figure 3. Similar to Chowdhury's[13] observations, RMAPP composites tend to absorb less water, although the water uptake trend remains obvious. The reason therefore is the fact that less hydroxyl groups at the fiber cell walls are available for reaction with water on the one hand, but the lumen, and herewith the capillary action remains present, on the other hand. A further consideration is that improved fiber/matrix binding characteristics eliminate cogitable space between fiber and matrix that would additionally tend to hold water.

Thermal stability

The results obtained by thermogravimetric analysis (TGA) are presented in Figure 4. The TGA curve of rice straw exhibits two mass-loss steps as also observed by Grozdanov et al.[6] The first weight loss takes place below 100°C and is related to the gradual evaporation of absorbed moisture. The second weight loss starts at 275°C and continues upon the decomposition of the major rice straw components (cellulose, hemicellulose and lignin). The PP matrix on the contrary mainly undergoes a single weight change step, where degradation rapidly takes place below 430°C, above which this

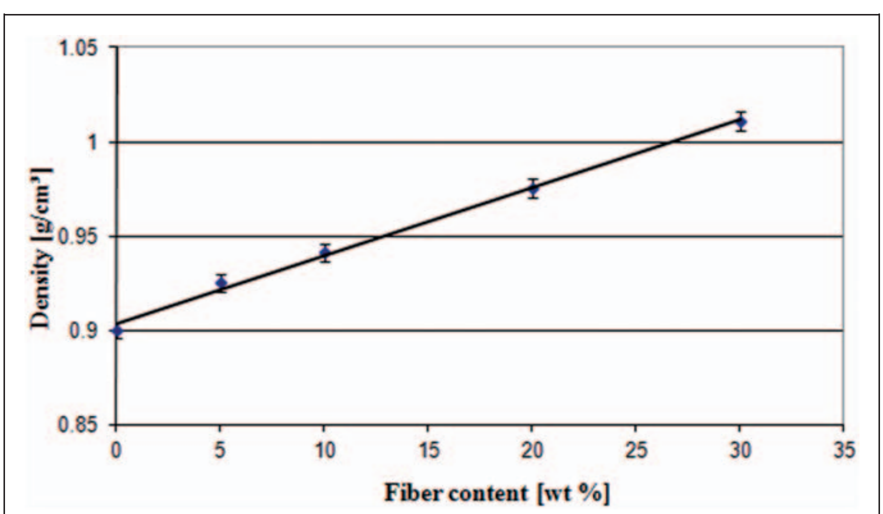

Figure 1. Density of RPP composites with varying fiber contents.

process occurs rapidly and is completed at around 470°C. According to Grozdanov et al.,[6] the thermal degradation of PP can take place through random chain scission and a radical chain mechanism.

Figure 4 further shows the evolution of the thermal stability of the RPP composites by means of TGA curves, related to the rice straw content. It can be seen that a change in the thermal behavior of relative to pure PP occurs upon the addition of natural fibers as observed by several other studies.[6,11] Thermal stability of composites can be observed up to 275°C, where thermal degradation of natural fibers starts. However, compared to the rice straw behavior, the thermal degradation rate of the incorporated fibers is cushioned by the surrounding PP. Accordingly, at around 430°C, the composite TGA curves again match with that of pure PP, where continued degradation takes place until it is completed at 470°C.

Observing the influence of rice straw content on the thermal behavior, it can be seen that upon increasing

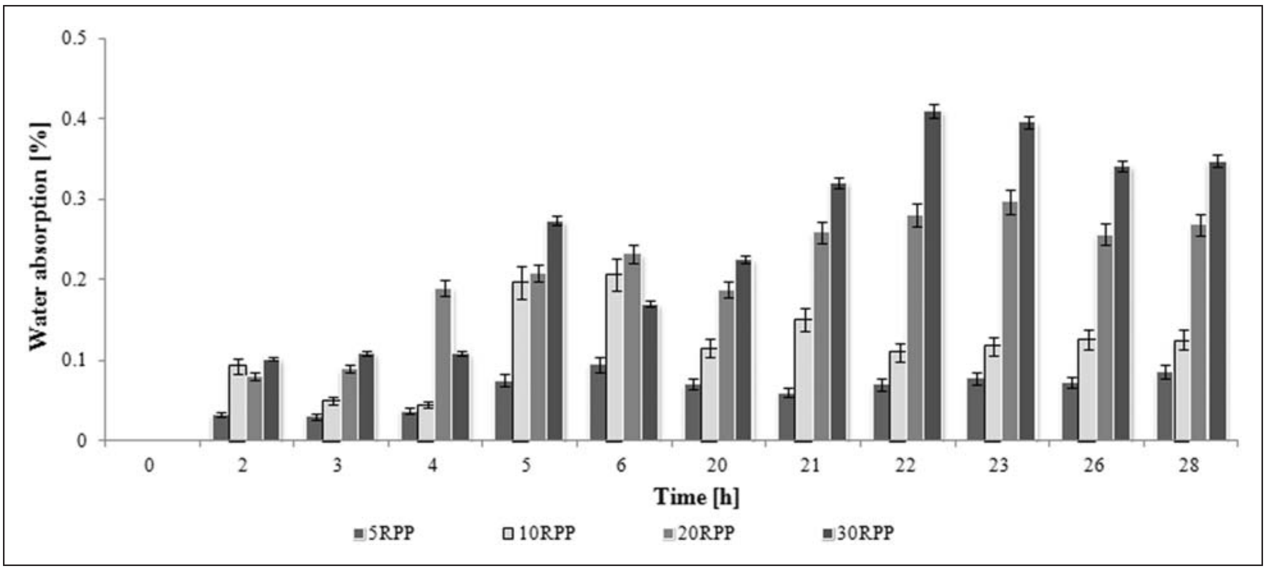

Figure 2. Water absorption behavior of RPP composites with respect to time.

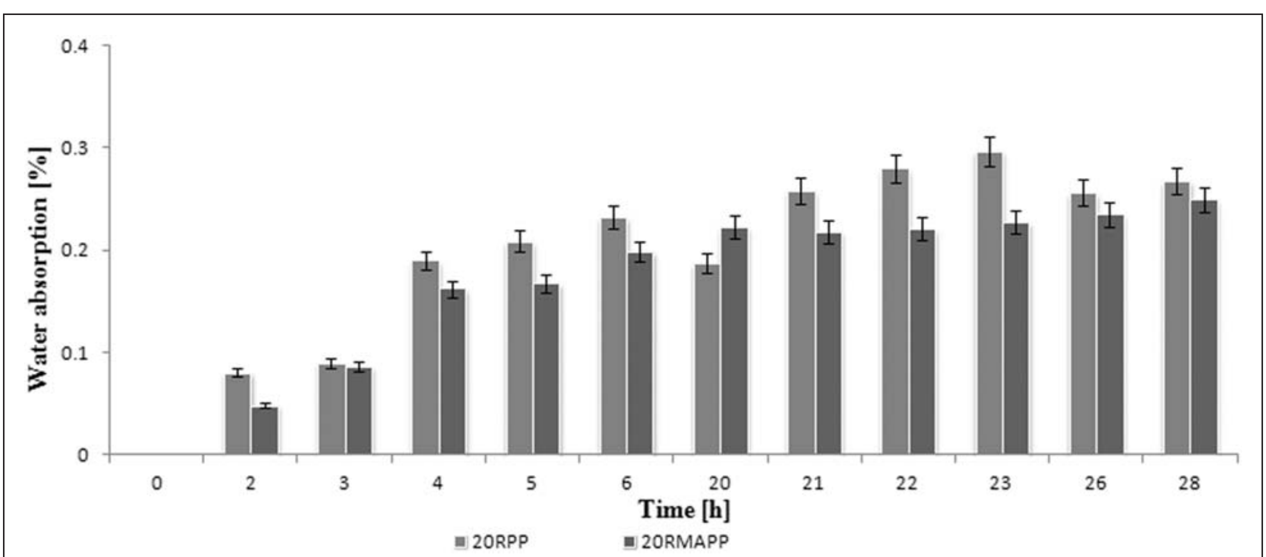

Figure 3. Water absorption behavior of 20 wt%.

fiber content, thermal degradation occurs earlier (i.e., at lower temperatures) on the one hand, whereas the curves become flattened (i.e., slower degradation rate) on the other hand. A similar change in the degradation pattern was also observed by Hujuri et al.[6,14] Generally, however, the increase of fiber content increases the amount of residues observed above 500°C. RMAPP composites show a similar thermal behavior related to the rice straw content, as presented in Figure 5. This is because the addition of coupling agent does not seem to have a large influence on the thermal behavior of natural fiber composites, as can be depicted from Figure 6.

Tensile properties

The results of tensile modulus, as presented in Figure 7, suggest that rice straw is able to impart greater stiffness to the composites. The addition of maleated polypropylene (MAPP) to polypropylene (PP) does not seem to have an influence on the stiffness behavior of the composites. Taha[15] suggests that stiffness does not primarily depend on the fiber–matrix interface, but more likely on the absolute fiber content in tensile loading direction, as the elastic modulus is determined as a tangent-modulus at low strain values (0.05–0.25%), where no

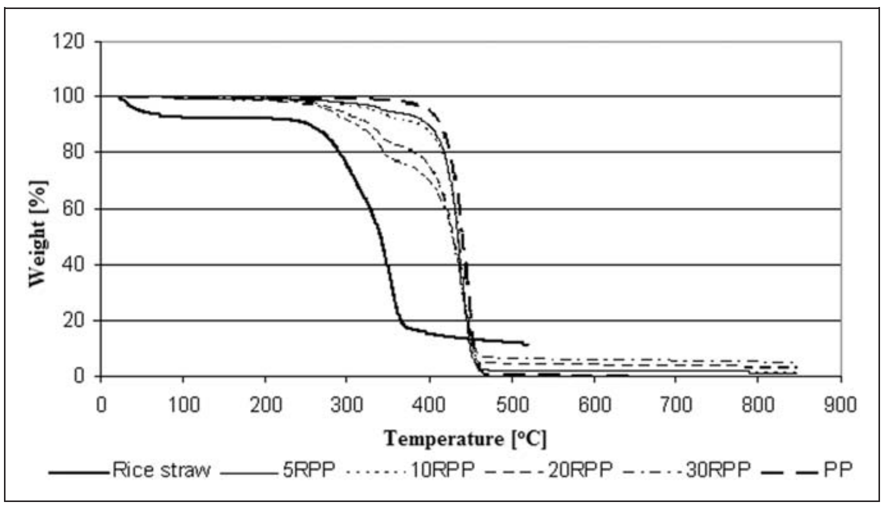

Figure 4. Effect of rice straw content on the thermal stability of RPP composites.

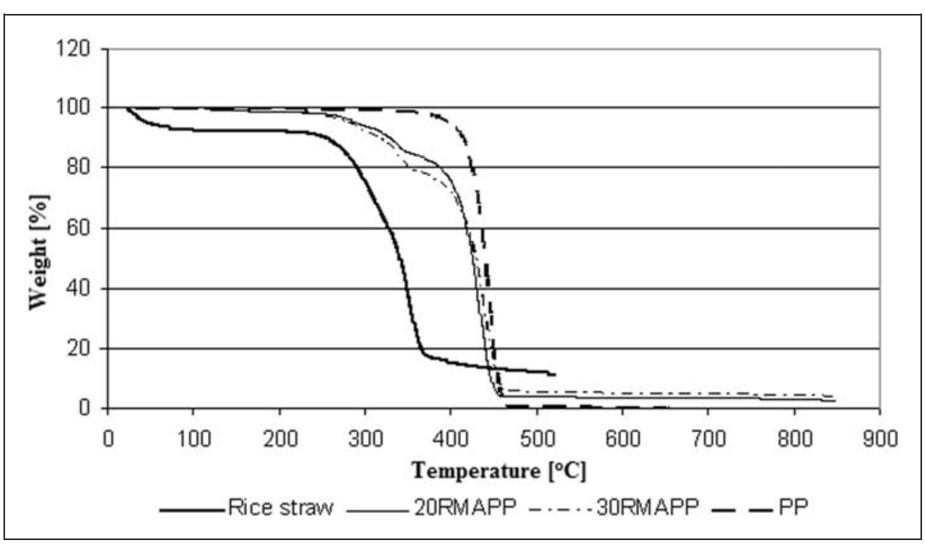

Figure 5. Effect of rice straw content on the thermal stability of RMAPP composites.

interfacial debonding is yet assumed to occur even in case of poor adhesion. Accordingly, intended improvement in the fiber/matrix bonding would not affect composite stiffness.

It is common to observe that an improvement in tensile modulus is at the expense of the fracture strain, as can be depicted in Figure 8 and as cited by several researchers.[15,16] The overlapping curves of RPP and RMAPP show that the failure strain witnesses a rapid fall from 500% to 6% upon fiber reinforcement from 0% to 5% by weight. Additional fiber reinforcement further lowers the failure strain of the composites, but not in the same rapid rate. Figure 8 illustrates a continuous decrease down to 0.8% at a fiber weight fraction of 30%. This behavior is observed for all fiber matrix combinations, although the rate in reduction of the elongation at break varied from case to case, depending on the polymeric matrix. Such behavior of more brittle fracture upon fiber reinforcement is supported by the fact that any impurities or voids confounding the matrix consistency would lead to material stiffening.

According to Albano et al.,[16] the incorporation of fillers into a thermoplastic matrix can increase or decrease the tensile strength of resulting composites. Figure 9 shows the behavior of tensile strengths of both RPP and RMAPP composites, where it becomes obvious that the addition of filling rice straw weakens

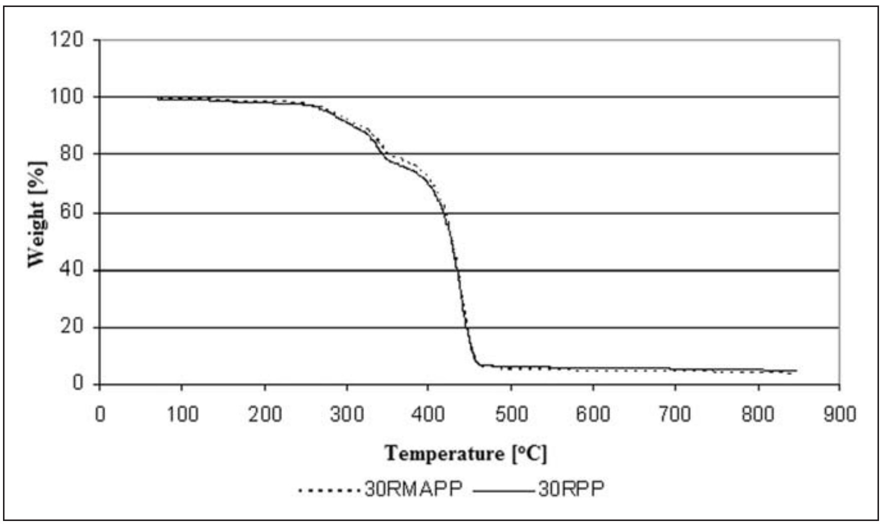

Figure 6. Effect of coupling agent on the thermal degradation of RPP composites.

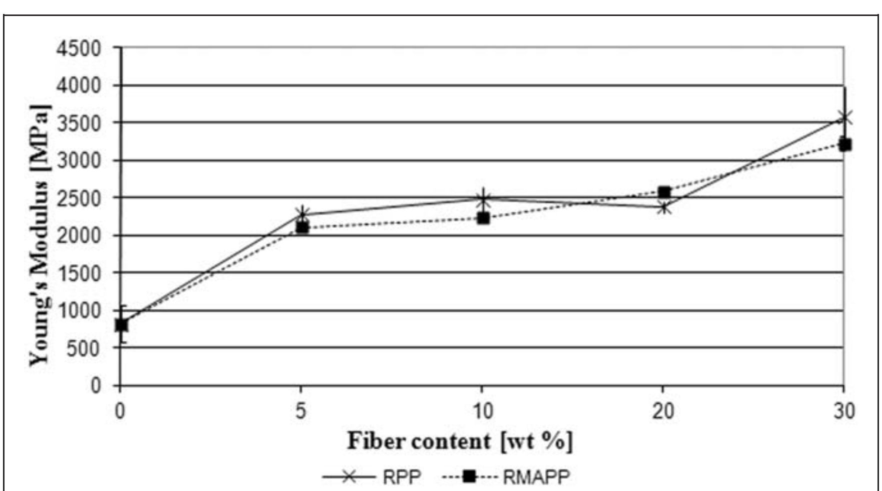

Figure 7. Effect of rice straw content on the stiffness of RPP and RMAPP composites.

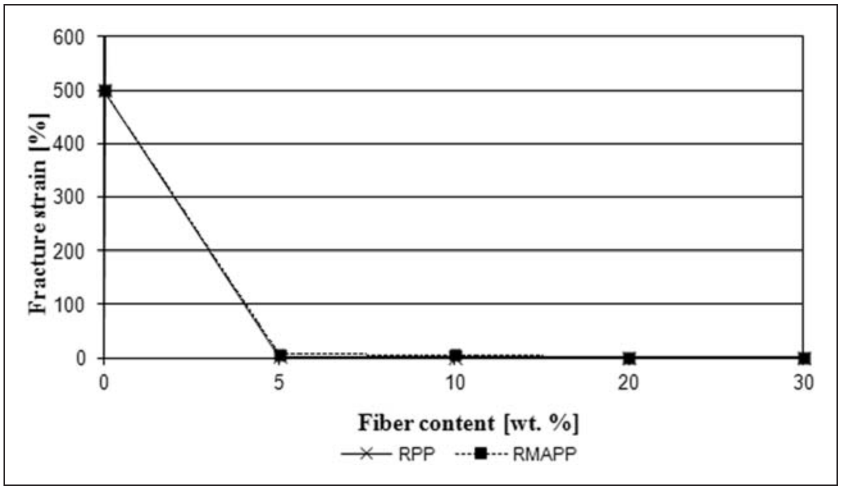

Figure 8. Effect of rice straw content on the fracture strain of RPP and RMAPP composites.

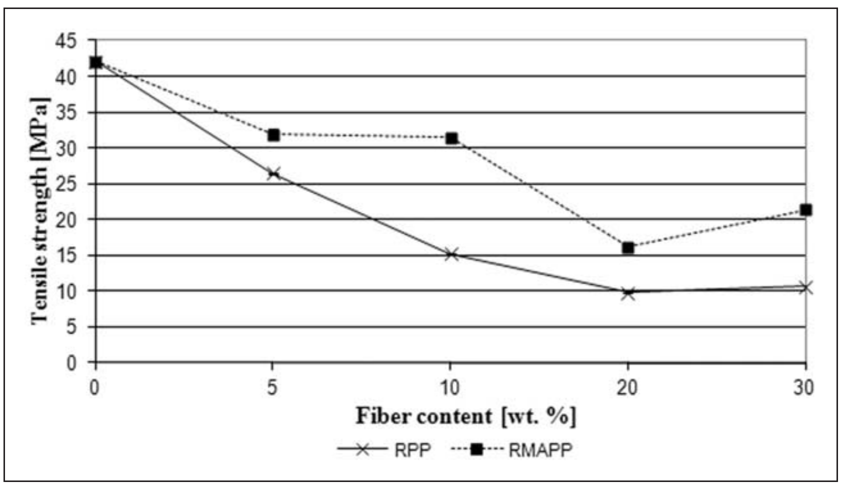

Figure 9. Effect of rice straw content on the tensile strength of RPP and RMAPP composites.

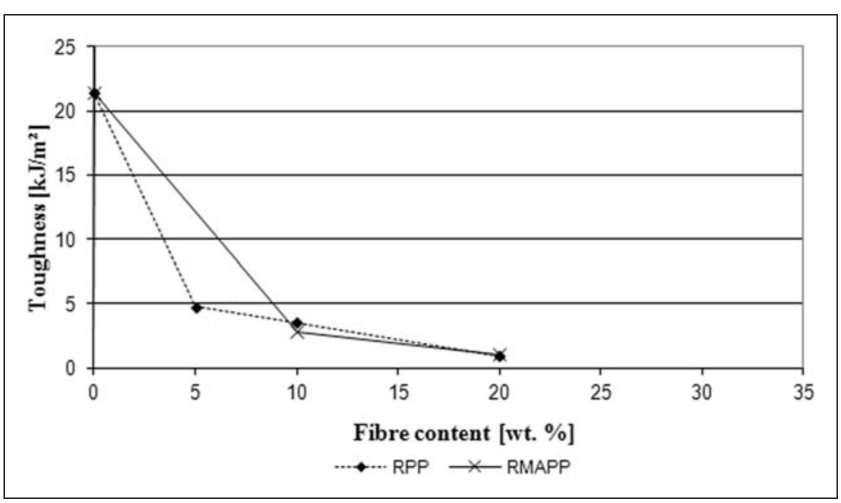

Figure 10. Impact strengths of RPP and RMAPP composites.

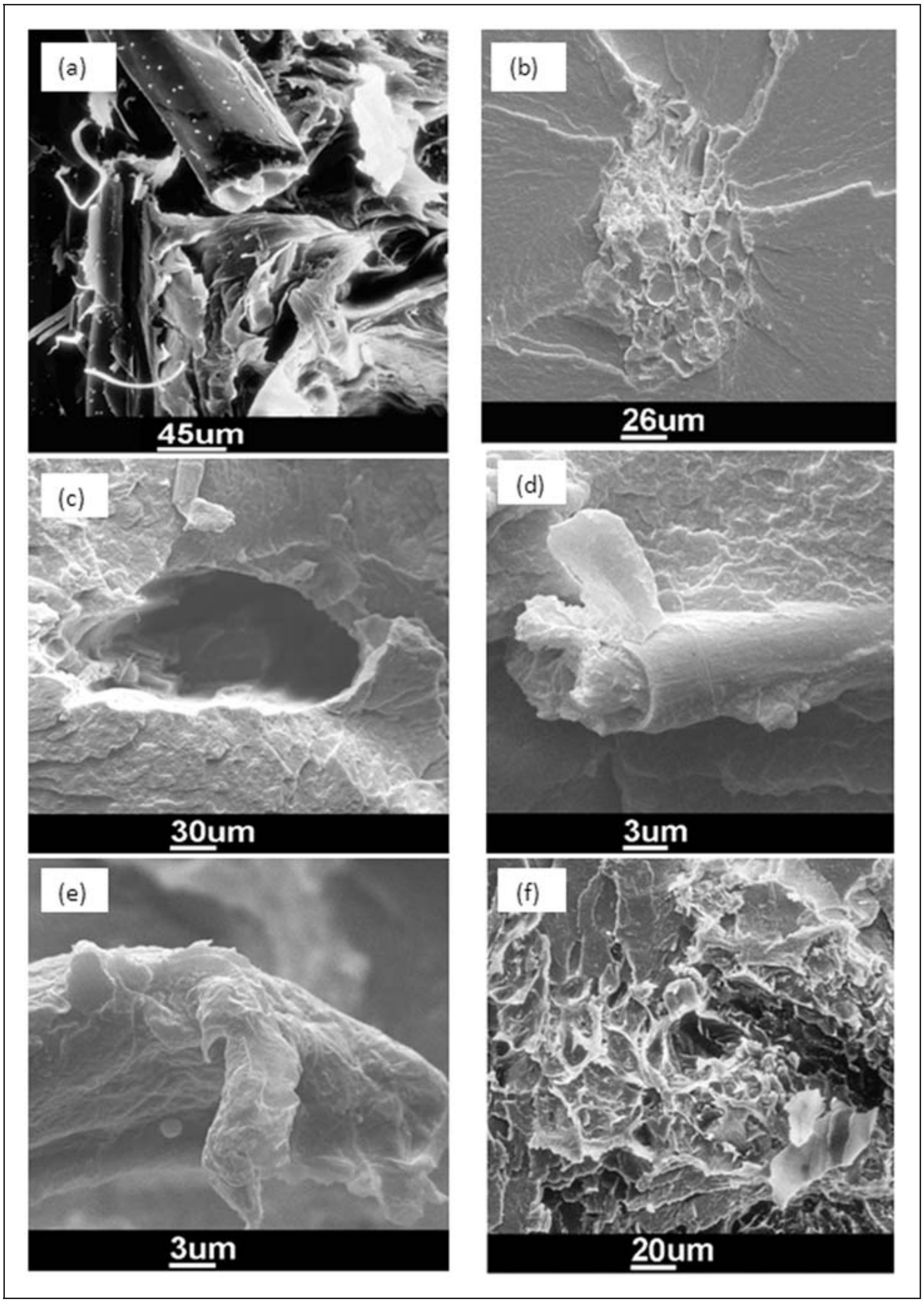

Figure 11. SEM micrographs of RPP (a–c) and RAMPP (d–f).

the matrix. Although several studies state a reduction in tensile strength at lower (between 0 wt% and 10 wt%) and again at higher (beyond 30 wt%) both RPP and RMAPP composites of this study seem to gradually loose strength upon the increase of rice straw content. This might be related to the filler shape. The dusty form of rice straw after grinding might have enhanced the formation of agglomerates, which can behave as higher size particles, reducing the adhesion effective surface,[17,18] which in turn implies a poor force transfer from the surrounding matrix to the reinforcement filler. Further studies can be made upon the variation of filler size and shape, as well as on the treatment of the rice straw itself to remove lignin, which is the main cause of such agglomeration problems. Taha et al.[15] describe the weakening effect of natural fibers at higher contents based on the agglomeration theory. A model based on the rule of mixtures allows the prognoses of reduced tensile strength based on fiber–matrix interfacial shear strength and composite processing conditions.

Despite the reduced tensile strength, however, the addition of maleated polypropylene to the matrix improves the fiber/matrix interface and results in higher tensile strength behavior of RMAPP compared to RPP, as illustrated in Figure 9.

Impact properties

Concerning the impact behavior of a composite material, there are various factors influencing the amount of absorbed impact energy. Impact strength of fiber-reinforced materials is primarily determined by the energy dissipated during fiber pull-out. This in turn is governed by a competition between fiber breakage and interface failure, and is thus determined both by the fiber tensile and interfacial shear strength. For natural fibers, it is to be noted that it is itself to be considered as a composite, meaning that internal fiber pull-out in terms of defibrillation as an additional source of energy dissipation. The results of impact testing reveal to increasing in impact strength of RMAPP compared to RPP, as can be depicted from Figure 10.

A sudden drop in impact strength occurs upon the addition of filling material, after which the strength level reveals minor changes. Djidjelli[10] reported similar observations and related these to the dilution effect: the higher the fiber content, the less ductile matrix is present in the system, leading to reduced composite toughness.

Scanning electron microscopy

Tensile fracture surfaces of the composites with and without maleic anhydride aid are shown in Figure 11(a–f).

It is observed that without the coupling agents (Figure 11(a)), rice straw was devoid of PP matrix, indicating a poor interfacial adhesion between the dispersed phase and the matrix. On the contrary, with the addition of coupling agents (Figure 11(e)), rice straw was coated by film layer (coupling agent) that efficiently increased its affinity to the PP.

It can be also noticed in Figure 11(b) that dispersion of untreated rice straw in the PP is poor where lignocellulosic materials tend to form agglomerates due to the presence of lignin; these agglomerates can lead to reduce the area of dispersed phase, reducing the adhesion effective surface.

Debonding of the fiber from the matrix is visible in Figure 11(c), where Figure 11(d) shows better interaction between rice straw and PP in the presence of coupling agent than the composite without process additives.

Rice straw surface is characterized as hydrophilic by polar hydroxyl groups and PP as hydrophobic by polyolefins. In the case of copolymers, which are maleic anhydride-grafted PPs, the anhydride groups of these modified PPs can link to the surface –OH groups of cellulose and its counterpart lignin through the formation of a block copolymer. This behavior could result in a higher reinforcing effect. On the other hand, the content of different amounts of maleic anhydride could result in significant variations in the coupling action, and thus influence the mechanical behavior.

Conclusions

The mechanical properties, thermal stability water absorption, and micromorphology of short rice straw reinforced PP composites was invistigated in this study. Here, the combined effect of the MAPP treatment as the compitilizer improved the interficial properties by strengthening fiber–polymer interaction, by enhancing fiber wetting and impregnating at the same time, by chemically binding the two surfaces. The impact properties of RMAPP was improved compared to RPP (between 5% and 10%). MAPP did not show a signifcant imrovement in the stiffness and tensile strength. General speaking, there was a marginal increase in the values of tensile modulus with increasing fiber contents. RMAPP composites tend to absorb less water than RPP. Maleic anhydride did not show a large influence on the thermal behavior of natural fiber composites.

There are a large scope for research in the field on natural fiber composites. Here, an effort has been made to observe the effect of chemical modification using MAPP on water absroption, thermal stability, and mechanical properties. In forthcoming communications, other coupling agents, biodegradability of PP – natural fiber copmosites will be the focus as the area of research. There can be a lot of imrovements in the properties of the composites by optimization of the fiber length, orientation, treatment procerdure, and appropriate coupling agents to optimize the interficial properties.

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